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Precise Synthesis of Exact Graft Polystyrenes with Branches from Two to Five in Number by Iterative Methodology Based on Living Anionic Polymerization

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ABSTRACT: The precise synthesis of a series of exact graft polystyrenes (PS)s with two, three, four, and five branches by a new iterative methodology based on living anionic polymerization is described. The methodology involves only three reaction steps in each iterative reaction sequence, i.e., (1) a transformation reaction of the 3-(*tert*-butyldimethylsilyloxy)propyl (SiOP) group into 3-bromopropyl function via deprotection of the silyl group, (2) a linking reaction of α-SiOP-ω-1,1-diphenylethylene (DPE)-functionalized polymer anion with α-terminal 3-bromopropyl-functionalized PS to prepare the backbone chain with the incorporation of a DPE moiety in the chain, and (3) an addition reaction of PSLi with the DPE moiety in the backbone to introduce a PS branch. By repeating the reaction sequence five times, we have succeeded in successively synthesizing a series of exact graft (PS)s having up to five branches for the first time. In the graft (PS)s all thus synthesized, not only the molecular weights of both backbone and branch chains but also the number and position of branch chains were precisely controlled.

Introduction

Graft (co)polymers have been studied for a long time as one of the representative branch polymers different in behavior and property from the corresponding linear polymers and as multiphase materials showing interesting morphologies in bulk and solution.[1,2] The following architectural parameters define a graft (co)polymer: (1) molecular weight of the backbone chain, (2) molecular weight of the branch chain, and (3) number and position of the branches along the backbone chain. In an ideal graft (co)polymer, such parameters are perfectly controlled.

The graft (co)polymer whose backbone and branch chains are controlled in molecular weight can be readily synthesized by the grafting onto method using the same (or different) living polymers as both backbone and branch chains.[1] The most generally studied synthetic procedure utilizes the linking reaction of functionalized backbone polymers via living anionic polymerization with premade living anionic polymers. The backbone functionalities that have been so far used include halomethyl, formyl, epoxy, ester, pyridinyl, and chlorosilyl functions.[2−4] The poly(2-chloroethyl vinyl ether) obtained by living cationic polymerization can also be used as an excellent functional backbone polymer because the molecular weight is controlled in a wide range up to 10^6 while keeping a narrow molecular weight distribution (M_w/M_n ∼1.1), and the 2-chloroethyl function is capable of linking with highly reactive living anionic polymers of styrene and isoprene.[5] Although the branch chains introduced via these functionalities are usually randomly distributed along the backbone chains, several highly dense graft (co)polymers with almost one branch in each monomer unit have recently been synthesized.[5−10]

Regarding the control of parameter 3, several graft copolymers with regularly spaced branch points were previously synthesized by the linking reaction of difunctional living anionic polymers with a macrolinking agent such as $(polystyrene)_2SiCl_2$, but the molecular weights of the backbone polymers were not controlled.[11−14] Furthermore, the method using such linking reactions does not allow different distances between the branch chains along the backbone polymers. Thus, even at the present time the control of parameter 3 still remains a challenging subject to be overcome in the precise synthesis of graft (co)polymers with ideal structures.

Great contributions to this subject have been made by Hadjichristidis and his co-workers. They were successful in synthesizing various well-defined π and H-shaped (co)polymers with two branches by the linking reaction of living anionic polymers with α,ω-functionalized polymers with the dichloromethylsilyl group as shown in Scheme 1.[2,15−20] In each of these (co)polymers, the distance between two branches corresponds to the molecular weight of the α,ω-functionalized polymer that can be controlled by the monomer to initiator ratio of the original living polymer. The positions of two branches along the backbone chain are determined by the molecular weights of the living anionic polymer to be linked and the α,ω-functionalized polymer. Similar well-defined H-shaped (co)polymers have recently been synthesized by the linking reaction of living anionic polymers with α,ω-functionalized polymers with two benzyl bromide moieties (see Scheme 1).[21,22] In such H-shaped (co)polymers, however, the positions of two branches are symmetric to each other and equidistant from the chain-ends.

In order to control the position of each branch chain, Hadjichristidis and his co-workers have developed an alternative stepwise synthesis of a well-defined graft copolymer with two branches by the methodology given in Scheme 2.[23] The first step was the 1:1 addition reaction of poly(isoprenyl)lithium (PILi) to 1,4-bis(phenylethenyl)benzene (PEB) to introduce a 1,1-diphenylethylene (DPE) moiety at the poly(isoprene) (PI) chain-end. Then, the resulting ω-terminal DPE-functionalized PI was reacted with a stoichiometric amount of poly(styryl)lithium

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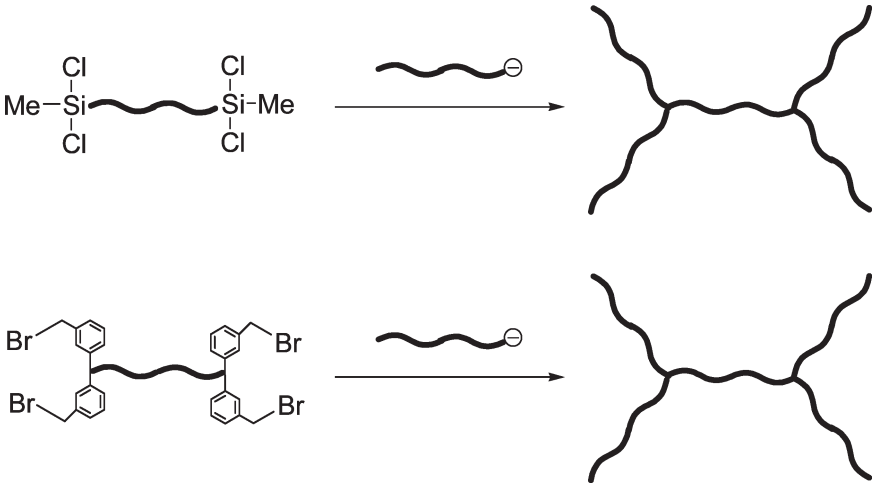
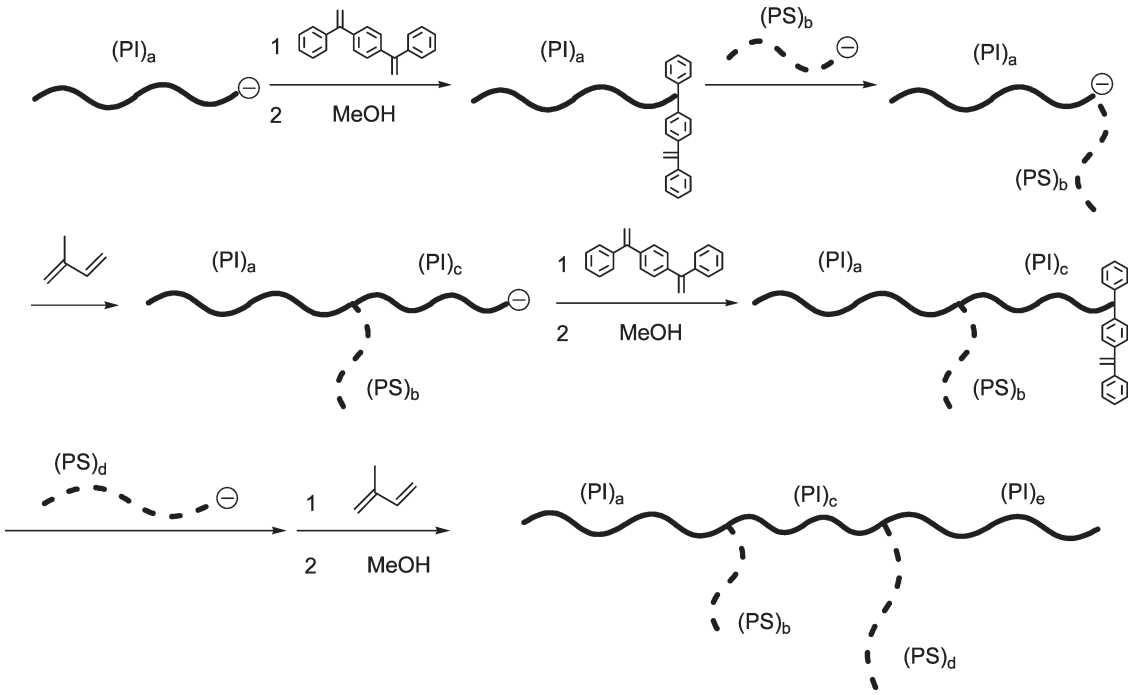
Scheme 1. Synthesis of H-Shaped Polymers



Scheme 2. Synthesis of an Exact Graft Copolymer Composed of Polystyrene and Poly(isoprene) Segments



(PSLi) to link the two polymer chains with the generation of a DPE-derived anion at the linking point. With use of this anion as a macroinitiator, isoprene was polymerized *in situ* to afford a living off-center graft copolymer with one PS branch, followed by reacting with a slight excess of PEB to introduce a DPE moiety at the chain-end. By repeating the same reaction sequence as shown in the scheme, the objective graft copolymer with two branches was successfully synthesized.

In the resulting graft copolymer, the distance between two PS branches exactly corresponds to the molecular weight of living PI initiated with the DPE-derived anion generated at the first linking point. The positions of the two PS branches are individually controlled by the molecular weights of living (PI)s obtained by the three polymerization steps. The ideal graft copolymer thus synthesized is named an exact graft copolymer by Hadjichristidis. Although the synthesis remains at the second stage, it may offer the potential for providing a general procedure for exact graft copolymers with more branches by further repeating the reaction sequence mentioned above. In this methodology, perfect stoichiometry, although practically difficult in experimental operation, is always required in each addition reaction of PSLi to the DPE moiety in the polymer chain.

Herein, we report the synthesis of a series of well-defined exact graft (PS)s with up to five PS branches by developing a new iterative methodology using a specially designed polymer anion coupled with a transformation reaction. The graft (PS)s synthesized in the present study satisfactorily fulfill the above-mentioned criteria, i.e., the control of all the parameters, 1, 2, and 3, required for exact graft (co)polymers.

Experimental Section

Materials. All chemicals (> 99% purity, special grades) were purchased from Aldrich, Japan, and used as received unless otherwise stated. Tetrahydrofuran (THF) was refluxed over Na wire for 12 h and distilled over $LiAlH_4$ under nitrogen atmosphere. It was finally distilled from its sodium naphthalenide solution on a high-vacuum line (10^{-6} torr). Heptane and *tert*-butylbenzene were washed with conc-H_2SO_4, water, and 10% NaOH (aq), dried over $CaCl_2$, and distilled over CaH_2 under reduced pressure. They were finally distilled from their

red-colored 1,1-diphenylhexyllithium solutions on the high-vacuum line. Both styrene and DPE were washed with 10% NaOH (aq), dried over $CaCl_2$, and distilled twice over CaH_2 under reduced pressure. They were finally distilled in the presence of Bu_2Mg (ca. 5 mol %) on the vacuum line into ampules equipped with break seals that were prewashed with *sec*-BuLi in heptane, diluted with *tert*-butylbenzene or THF via the high-vacuum technique, and subdivided into ampules equipped with break seals that were prewashed with *sec*-BuLi in heptane. *N*,*N*,*N*′,*N*′-Tetramethylethyenediamine (TMEDA) was distilled twice over CaH_2 under nitrogen atmosphere and finally distilled in the presence of BuLi on the vacuum line. 3-(*tert*-Butyldimethylsiloxy)-1-propyllithium (SiOPLi) in cyclohexane (15 wt %) purchased from FMC Corporation, Lithium Division, was diluted with heptane and subdivided via the high-vacuum technique. 1,4-Bis(phenylethenyl)benzene (PEB) was synthesized according to the procedure previously reported.[24] After recrystallization from ethyl acetate (mp. 137 °C), PEB was diluted with THF and subdivided via the high-vacuum technique.

Measurements. Both ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $CDCl_3$ (δ 7.26 for ^{1}H NMR and δ 77.1 for ^{13}C NMR). Size exclusion chromatography (SEC) and right angle laser light scattering (RALLS) were measured on an Ashahi Techneion Viscotek Model 302 TDA with triple detector software. Three detectors, right angle laser light scattering (λ = 670 nm, Power = 3 mW), RI, and UV (λ = 254 nm) detectors, and a viscometer were used. The dn/dc values were automatically measured by this instrument. In order to make sure of these values, they were also separately measured with an Ohotsuka Electronics DMR-1020 refractometer operating at 633 nm. THF was used as an eluent at a flow rate of 1.0 mL/min at 30 °C. Three polystyrene gel columns (pore size (bead size): 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm)) were used. Absolute molecular weights ($M_{w\ RALLS}$) were calculated using the triple detector software.

Synthesis of Exact Graft (PS)s. Except for the deprotection and transformation reactions, all of the polymerizations and linking and addition reactions were carried out under high-vacuum conditions (10^{-6} torr) in sealed glass reactors equipped with break seals. The reactors were always sealed off from the vacuum line and then prewashed with a red-colored 1,1-diphenylhexyllithium (ca. 0.05 M) in heptane solution prior to the polymerizations and reactions. All operations were performed according to the usual high-vacuum technique reported elsewhere.[25]

A series of exact graft (PS)s were synthesized stepwise by repeating the same reaction sequence involving the following three reaction steps: (1) a transformation reaction of 3-(*tert*-butyldimethylsilyloxy)propyl (SiOP) group to 3-bromopropyl function used as a new reaction site via deprotection of the silyl group, (2) a linking reaction to prepare the backbone chain with the incorporation of a DPE moiety, and (3) an addition reaction to introduce the branch chain. In each of the reaction sequences, the three reactions were performed as follows: The SiOP terminus of PS was first deprotected with a 50-fold molar excess of $(C_4H_9)_4NF$ in THF at 25 °C for 12 h. The resulting 3-hydroxypropyl group was transformed into 3-bromopropyl function by treatment with a 50-fold molar excess of CBr_4 and Ph_3P in CH_2Cl_2 at 25 °C for 12 h under an atmosphere of nitrogen. In each reaction, the polymer solution was adjusted to be ca. 10 wt %, and the reaction mixture was poured into methanol to precipitate the polymer. The resulting polymer was reprecipitated twice from the THF solution to methanol and freeze-dried from its absolute benzene solution for 24 h. Although the deprotection and transformation reactions were observed by ^{1}H NMR analyses to be quantitative within experimental errors, the polymers were isolated in around 90% yields after the two reprecipitation steps.

Both the linking and addition reactions were carried out under high-vacuum conditions using sealed reactors with break seals. In the linking reaction, a 2.0-fold excess of an α-SiOP-ω-DPE-functionalized polymer anion (10 wt % in *tert*-butylbenzene and THF (1/1, v/v)) was reacted with chain-end-functionalized PS with a 3-bromopropyl group (10 wt % in THF) at −78 °C for 5 min and then at 25 °C for 12 h. The α,ω-functionalized polymer anion was prepared as follows: Styrene (2 M in *tert*-butylbenzene) was polymerized with SiOPLi (0.05 M in heptane) in the presence of three or more equivalents of TMEDA at 0 °C for 0.5 h and 25 °C for an additional 1 h. Then, the living PS solution was cooled to −78 °C, and an equal amount of THF was added, followed by reacting with a 1.5-fold molar excess of PEB in THF (5 wt %) at −78 °C for 0.5 h. The linking reaction was terminated with degassed methanol, and the reaction mixture was poured into a large excess of methanol to precipitate the polymer. The objective polymer was isolated by fractional precipitation, reprecipitated two more times from the THF solution to methanol, and freeze-dried from the absolute benzene solution. The resulting α-SiOP-in-chain-DPE-functionalized PS (10 wt % in THF) was then reacted with a 1.5-fold molar excess of PSLi (10 wt % in THF) under the conditions at −78 °C for 12 h. Thus, the PS branch was introduced by this addition reaction. The reaction was terminated with degassed methanol, and the reaction mixture was poured into a large excess of methanol to precipitate the polymer. The objective polymer was isolated by fractional precipitation, reprecipitated two more times from the THF solution to methanol, and freeze-dried from the absolute benzene solution.

The polymer mixtures obtained by the reactions were always monitored by SEC to follow the reactions, and the reaction efficiencies were determined by comparing the two SEC peak areas of the objective polymers and the excess living polymers to be reacted. Finally, the objective polymers were isolated by fractional precipitation using cyclohexane and hexane mixtures as follows: Around 0.5 wt % polymer was dissolved in cyclohexane, and hexane was then added slowly to the cyclohexane solution until the solution became slightly cloudy, followed by cooling the mixture to 0 °C to allow for 1 h. In this operation, (PS)s with higher than 10 000 g/mol in M_n value were precipitated, while (PS)s with M_n values lower than 10 000 g/mol remained in solution. The polymers were generally isolated in more than 80% yields by fractional precipitation. The same reaction sequence was repeated under the same conditions. The details are described in the next section.

Synthesis of 3-Arm Star-Branched PS with One PS Arm with a SiOP Terminus. The title 3-arm star-branched PS synthesized by the above-mentioned three reaction steps is a minimum unit of the exact graft PS, and therefore, the synthetic route is described in detail as a representative. Chain-end-functional PS with a SiOP group was prepared by the living anionic polymerization of styrene (23.9 mmol) in *tert*-butylbenzene (11.6 mL) with SiOPLi (0.242 mmol) and TMEDA (0.770 mmol) in heptane (1.38 mL) under the conditions at 0 °C for 0.5 h and then at 25 °C for an additional 1 h. After quenching with degassed methanol under vacuum, the polymer was precipitated in methanol, purified by reprecipitation twice from the THF solution to methanol, and freeze-dried from its absolute benzene solution for 24 h (2.46 g, 100% yield, M_n (SEC) = 10 200 g/mol, M_w/M_n = 1.02). The degree of end-functionalization was virtually quantitative by comparing the resonance signal areas of Si-CH_3 protons at 0.01 ppm with that of either PS phenyl protons at 6.3−7.2 ppm.

The resulting polymer (2.46 g) dissolved in THF (25.0 mL) was treated with $(C_4H_9)_4NF$ (12.0 mmol) in THF (12.0 mL) at 25 °C under nitrogen atmosphere. The reaction mixture was stirred for 12 h and poured into methanol to precipitate the polymer. The polymer was reprecipitated twice and freeze-dried from its absolute benzene solution (2.30 g, 93% yield, M_n (SEC) = 10 100 g/mol, M_w/M_n = 1.02). Complete deprotection was confirmed by the disappearance of signals for Si-CH_3 and C-CH_3 protons at 0.01 and 0.86 ppm, respectively. The resulting

α-functionalized PS with the 3-hydroxypropyl group (2.30 g), CBr_4 (11.3 mmol), and Ph_3P (11.6 g, mmol) was dissolved in THF (25.0 mL) under nitrogen atmosphere. The mixture was stirred at 25 °C for an additional 12 h and poured into a large amount of methanol to precipitate the polymer. The polymer was reprecipitated twice from the THF solution to methanol and freeze-dried from its absolute benzene solution for 24 h (2.07 g, 90% yield, M_n (SEC) = 10 200 g/mol, M_w/M_n = 1.02). The degree of end-functionalization was quantitative by comparing the resonance signal areas of Br-CH_2 protons at 3.23 ppm with that of PS phenyl protons at 6.3−7.2 ppm. The quantitative transformation was also confirmed by the observation that the signal for CH_2 protons was completely shifted from 3.46 to 3.23 ppm. Thus, α-functionalized PS with the 3-bromopropyl group was successfully prepared.

Styrene (40.8 mmol) in *tert*-butylbenzene (19.9 mL) was polymerized with SiOPLi (0.416 mmol) and TMEDA (1.44 mmol) in heptane (2.57 mL) at 0 °C for 0.5 h and 25 °C for an additional 1 h. The living polymer solution was cooled to −78 °C, and THF (34.0 mL) was added. Then, PEB (0.680 mmol) in THF (8.29 mL) was added to the living polymer solution, and the mixture was allowed to stand at −78 °C for 0.5 h. Then, the α,ω-functionalized polymer anion (4.24 g) thus prepared was reacted with the chain-end-functionalized PS with the 3-bromopropyl group (1.95 g) in THF (19.0 mL) at −78 °C for 5 min. The reaction mixture was warmed to 25 °C for an additional 12 h, quenched with degassed methanol, and poured into methanol to precipitate the polymers. The linking efficiency was determined to be virtually quantitative on the basis of the SEC peak areas of the linked polymer and the α,ω-functionalized polymer anion used in excess. The objective linked polymer was isolated by fractional precipitation using a mixture of cyclohexane and hexane, reprecipitated twice, and freeze-dried (3.18 g, 85%, M_n (SEC) = 19 600 g/mol, M_w/M_n = 1.02). The ^{1}H NMR signals at 5.40, 0.86, and 0.01 ppm corresponding to CH_2=C protons of the DPE moiety and C-CH_3 and Si-CH_3 protons of the initiator residue were observed at reasonable ratios.

In order to synthesize a 3-arm star-branched PS, PSLi (0.164 mmol, M_n (SEC) = 8 920 g/mol, M_w/M_n = 1.02) prepared by the polymerization of styrene (1.46 g, 14.2 mmol) with *sec*-BuLi (0.164 mmol) in THF (15.0 mL) at −78 °C for 0.5 h was added to the above polymer (2.04 g, 1.04 mmol) dissolved in THF (20.1 mL) at −78 °C. The reaction mixture was allowed to react at −78 °C for 12 h and quenched with degassed methanol. The polymer was precipitated in methanol, reprecipitated twice, and freeze-dried. The objective 3-arm star-branched PS was isolated by fractional precipitation, reprecipitated twice, and freeze-dried (2.73 g, 90%, M_n (RALLS) = 29 200 g/mol, M_w/M_n = 1.02).

Starting from the 3-arm star-branched PS thus synthesized, the same reaction sequence involving the three reaction steps was repeated four times to afford a series of exact graft (PS)s with two, three, four, followed by five branches. Each of the three reactions and isolation and purification of the objective polymer were carried out under the above-mentioned conditions. Amounts of the starting 3-arm star-branched PS, exact graft (PS)s with two, three, and four branches were 2.10 g, 1.85 g, 1.62 g, and 1.14 g, respectively, while those of the objective exact graft (PS)s with two, three, four, and five branches, after purification and isolation, were 2.08 g, 1.75 g, 1.24 g, and 1.04 g, respectively. All of the polymers were carefully characterized by ^{1}H and ^{13}C NMR, FT-IR, SEC, and RALLS. Their molecular weights and molecular weight distributions are listed in Tables 1 and 2. ^{1}H NMR chemical shifts of the resulting exact graft (PS)s are very similar to each other except for the peak area of the terminal SiOP group. The following ^{1}H NMR chemical shifts in $CDCl_3$ are those of the exact graft PS with five branches as a representative: δ 7.2−6.3 (m, aromatic), 3.46 (s, Si-CH_2-O-), 2.3−1.1 (m, -CH_2-CH-), 0.86 (s, -Si-C(CH_3)$_3$), 0.01 (s, Si(CH_3)$_2$).

Table 1. Characterization Results of Prepolymer, Intermediate polymers, and Exact Graft Polystyrenes (PS)s with One and Two PS Branches

	$M_n \times 10^{-3}$ (g/mol)			$M_w \times 10^{-3}$ (g/mol)		
polymer	calcd	SEC	RALLS	calcd	RALLS	M_w/M_n
SiOP-PS[a]	10.4	10.2		10.6		1.02
SiOP-PS-D-PS[b]	20.6	19.6	19.6	21.0	19.9	1.02
EG-1[c]	29.1	26.9	29.2	29.7	29.8	1.02
EG-1-D[d]	39.0	36.4	40.9	39.8	41.7	1.02
EG-2[e]	51.2	45.0	54.3	52.2	55.4	1.02

[a] α-Terminal SiOP-functionalized PS. [b] α-SiOP-in-chain-DPE-functionalized PS. [c] Exact graft PS with one PS branch (3-Arm star-branched PS). [d] Exact graft PS with one PS branch and in-chain-DPE functionality. [e] Exact graft PS with two PS branches.

Table 2. Characterization Results of Intermediate and Exact Graft Polystyrenes (PS)s with Three, Four, and Five PS Branches

	$M_n \times 10^{-3}$ (g/mol)			$M_w \times 10^{-3}$ (g/mol)		
polymer	calcd	SEC	RALLS	calcd	RALLS	M_w/M_n
EG-2-D[a]	73.5	61.0	73.7	75.0	75.2	1.02
EG-3[b]	83.5	65.1	84.1	85.2	85.8	1.02
EG-3-D[c]	89.5	71.7	90.6	92.2	93.3	1.03
EG-4[d]	102	78.5	103	105	106	1.03
EG-4-D[e]	114	89.6	114	117	117	1.03
EG-5[f]	125	94.7	124	129	128	1.03

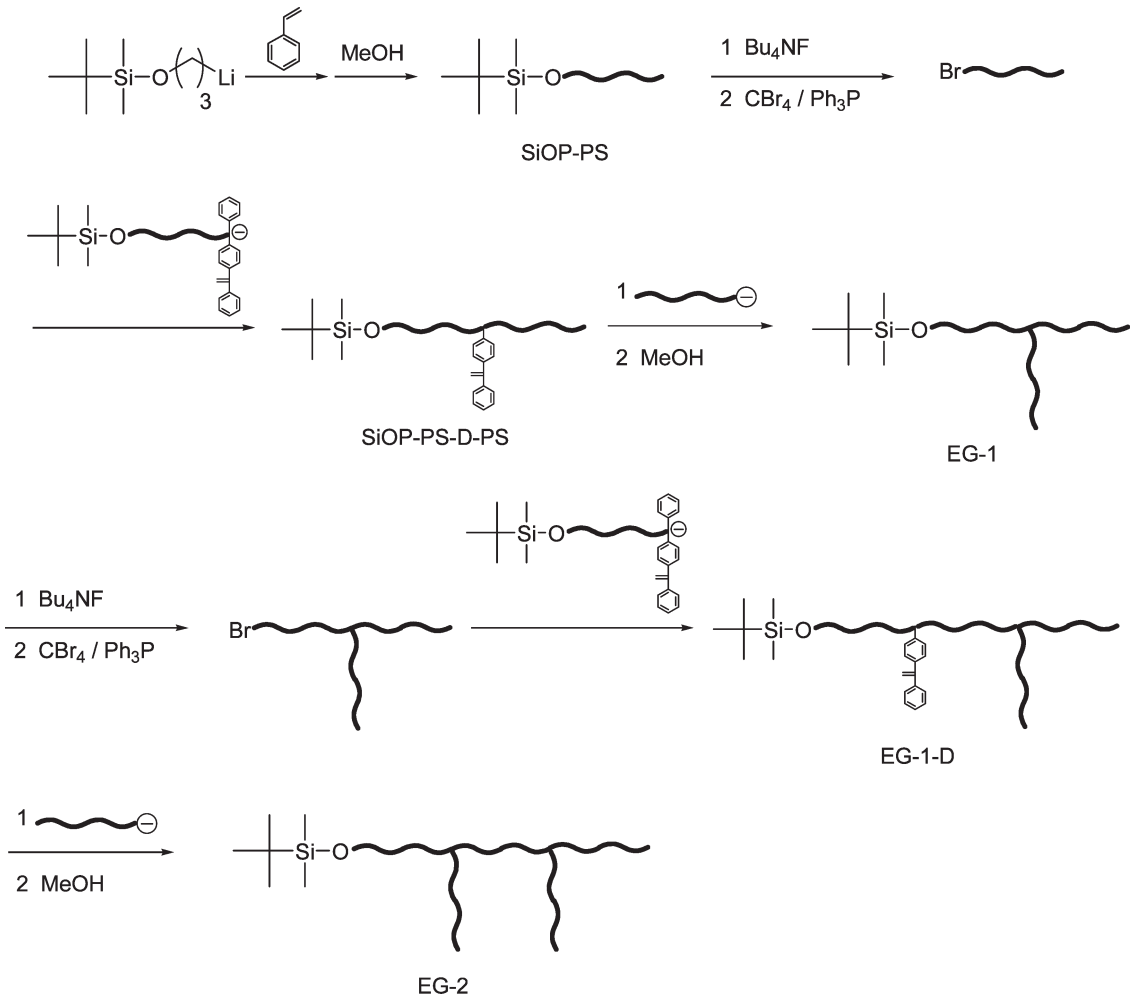
[a] Exact graft PS with two PS branches and in-chain-DPE functionality. [b] Exact graft PS with three PS branches. [c] Exact graft PS with three PS branches and in-chain-DPE functionality. [d] Exact graft PS with four PS branches. [e] Exact graft PS with four PS branches and in-chain-DPE functionality. [f] Exact graft PS with five PS branches.

Results and Discussion

Synthesis of Exact Graft PS with Two Branches. Although there is a similarity between the methodologies reported by Hadjichristidis et al.[23] and that developed herein by us, the fundamental difference is that our methodology is based on the termination method to construct both backbone and branch chains, while the initiation method is used to prepare the backbone chain in the methodology by Hadjichristidis et al. Moreover, in order to prepare the reaction site needed in the next linking reaction, a transformation reaction is employed in each reaction sequence as an extra reaction step in our methodology. The reason will be described later.

The synthetic route of an exact graft PS with two branches by our methodology is illustrated in Scheme 3. The first stage of the synthesis is the preparation of a 3-arm star-branched PS having one PS arm with a SiOP terminus (EG-1). Styrene was first polymerized with SiOPLi in the presence of TMEDA in *tert*-butylbenzene at 0 °C for 0.5 h and then at 25 °C for an additional 1 h. In this polymerization, the presence of three or more equivalents of TMEDA toward SiOPLi was essential to narrow the molecular weight distribution. The resulting α-terminal SiOP functionalized PS (SiOP-PS) was precisely controlled in molecular weight as was seen in Table 1. The terminal SiOP group was then transformed into 3-bromopropyl function by treatment with $(C_4H_9)_4NF$, followed by reacting with Ph_3P and CBr_4. The end-functionalization degree was observed by ^{1}H NMR to be quantitative. The characteristic resonances for Si-CH_3 and C-CH_3 protons at 0.01 and 0.86 ppm as well as CH_2-OSi protons at 3.46 ppm in the original polymer completely disappeared and a new signal for CH_2-Br protons at 3.23 ppm appeared at the reasonable peak area.

Scheme 3. Successive Synthesis of Exact Graft (PS)s with One and Two Polystyrene Branches (Exact Graft-1(EG-1) and EG-2) by Iterative Methodology



Next, an α-SiOP-ω-DPE-functionalized polymer anion was prepared by the same anionic polymerization of styrene with SiOPLi in the presence of TMEDA, followed by reacting with a 1.5-fold excess of PEB at −78 °C. Similar to the addition reaction of PEB to either of the living anionic polymers of styrene and isoprene previously reported,[23,26] only one of the two double bonds of PEB reacted with the α-SiOP-functionalized PSLi as was seen in Scheme 3. The quantitative incorporation of both SiOP and DPE functionalities into PS was confirmed by ^{1}H NMR analysis. Then, a 2.0-fold excess of the α,ω-functionalized polymer anion thus prepared was reacted *in situ* with the α-terminal 3-bromopropyl functionalized PS to link the two PS chains under the conditions in a mixture of *tert*-butylbenzene and THF (1/2, v/v) at −78 °C for 5 min and at 25 °C for 12 h. As shown in Figure 1a, the SEC profile of the reaction mixture exhibits only two distinct sharp peaks corresponding to the linked product and the deactivated α,ω-functionalized polymer anion used in excess in the reaction. The linking efficiency was estimated to be quantitative by comparing the two SEC peak areas. The linked product was isolated in 85% yield by fractional precipitation using a mixture of cyclohexane and hexane (see Figure 1b). The expected structure of the isolated polymer was confirmed by SEC-RALLS (M_n value) and ^{1}H NMR (SiOP and DPE functionalities), respectively, as listed in Table 1. Thus, the α-terminal SiOP and in-chain-DPE-functionalized PS (SiOP-PS-D-PS) was obtained.

In the final step of the reaction sequence, a 1.5-fold excess of PSLi was added to react with the DPE moiety incorporated in the above-prepared polymer in THF at −78 °C for 12 h to introduce the PS arm segment. As shown in Figure 2a, the SEC profile of the reaction mixture exhibits only two peaks corresponding to the 3-arm star-branched PS and the deactivated PSLi used in the excess in the reaction. The objective star-branched polymer was isolated in 90% yield by fractional precipitation and found to possess a sharp monomodal SEC distribution (see Figure 2b). The molecular weight determined by RALLS was in good agreement with that expected (see Table 1). Thus, the three reaction steps (transformation, linking, and addition reactions) in the reaction sequence proceeded cleanly and virtually quantitatively to result in the formation of the corresponding three polymers, i.e., α-terminal 3-bromopropyl-functionalized PS, α-SiOP-in-chain-DPE-functionalized PS (SiOP-PS-D-PS), and 3-arm star-branched PS with one PS arm with a SiOP terminus (EG-1). Since the 3-arm star-branched PS has the same SiOP terminus as the starting α-terminal SiOP-functionalized PS, the same reaction sequence can be repeated. Thus, this star-branched PS is used as the starting material for the next graft PS with two branches and therefore regarded as a minimum unit of the exact graft PS series targeted in the present synthesis.

The same reaction sequence was actually repeated with use of the 3-arm star-branched PS as starting material. In the

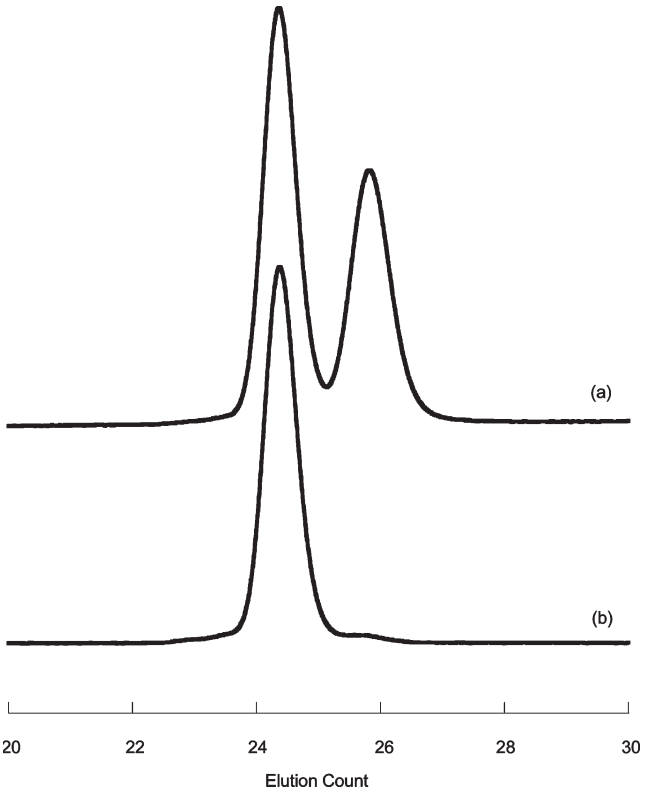


Figure 1. Size exclusion chromatographic profile of the reaction mixture (a) and the isolated α-terminal 3-*tert*-butyldimethylsilyoxypropyl and in-chain-DPE-functionalized polystyrene (b).

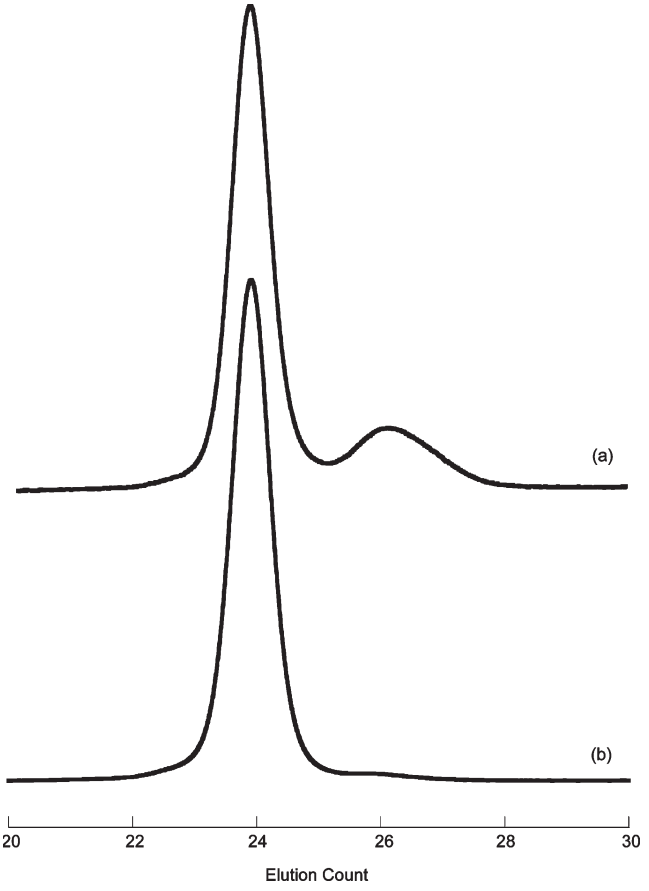


Figure 2. Size exclusion chromatographic profile of the reaction mixture (a) and the isolated 3-arm star-branched polystyrene abbreviated as EG-1 (b).

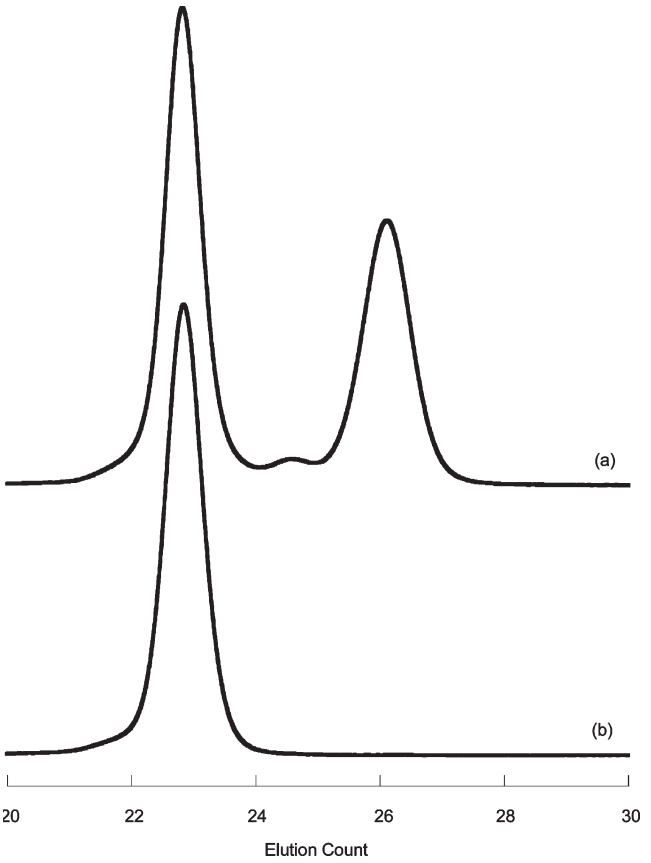
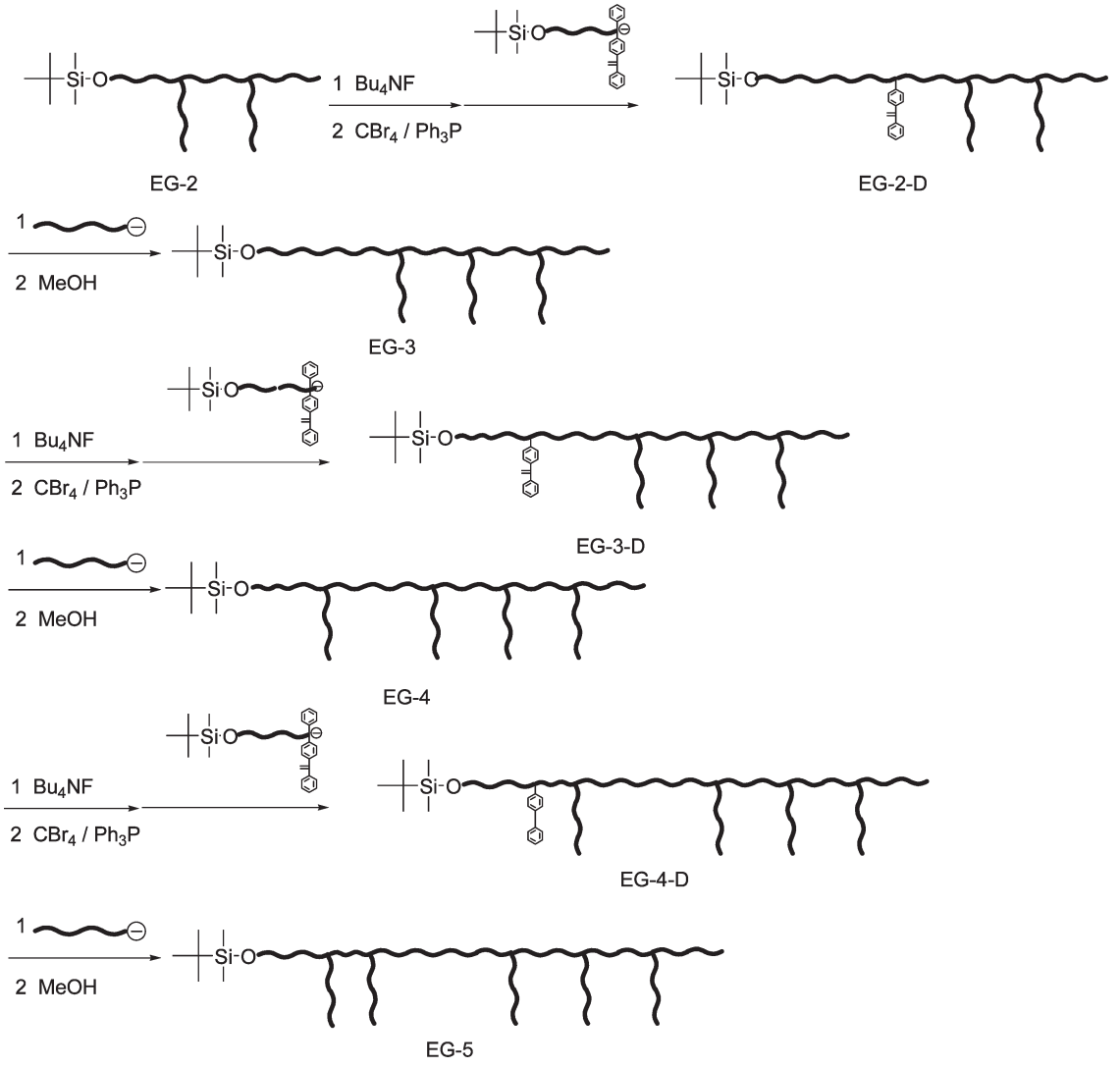


Figure 3. Size exclusion chromatographic profile of the reaction mixture (a) and the isolated exact graft polystyrene with two polystyrene branches (EG-2) (b).

first step, the terminal SiOP group of the 3-arm star-branched PS was transformed into the 3-bromopropyl group under conditions identical to those mentioned above. The SEC profiles of the polymers before and after the transformation reaction were almost the same in shape and distribution. Quantitative end-functionalization was confirmed by ^{1}H NMR analysis. The α-SiOP-ω-DPE-functionalized polymer anion was again prepared and reacted with the brominated star-branched PS to link the two chains. Similar to Figure 1a, only two sharp SEC peaks were observed for the linked product and the deactivated α,ω-functionalized polymer anion used in excess.[27] Importantly, neither high molecular weight product nor the brominated polymer was observed at all. The linked polymer (EG-1-D), isolated by fractionation, possessed the expected molecular weight and a narrow molecular weight distribution (see Table 1). For the synthesis of a graft PS with two PS branches, PSLi was reacted with the DPE moiety in the polymer chain to introduce the second PS branch. The reaction was monitored by SEC and found to proceed as desired as shown in Figure 3a. The graft polymer isolated by fractional precipitation exhibited sharp monomodal SEC distributions, free of their precursor polymers (see Figure 3b). The results are also summarized in Table 1. As you can see, the molecular weight is in good agreement with that calculated, and a narrow molecular weight distribution is attained. All of the analytical results clearly indicate the successful formation of the exact graft PS with two branches whose positions are precisely controlled as desired. Thus, it is proved that the α-SiOP-ω-DPE-functionalized polymer anion is a key material specially designed in order to simultaneously introduce both the reaction sites as well as to prepare the backbone chain.

Scheme 4. Successive Synthesis of Exact Graft (PS)s with Three, Four, and Five PS Branches (EG-3, EG-4, and EG-5) by Iterative Methodology



The resulting exact graft PS with two branches (EG-2) was purified, dried carefully, and used as the starting material in the next reaction stage.

Synthesis of Exact Graft (PS)s with Three, Four, and Five Branches. Scheme 4 shows the stepwise synthesis of the graft (PS)s with three, four, and five branches by repeating the same reaction sequence three times. In order to demonstrate the possible control of the branch positions, the distances between the third and fourth branches and the fourth and fifth branches are designed to be around 20 000 and 6000 g/mol in molecular weight, respectively. Therefore, the molecular weights of the α-SiOP-ω-DPE-functionalized polymer anions were adjusted according to this purpose. Starting from the graft PS with a SiOP terminus, the transformation to 3-bromopropyl function, the linking reaction of the brominated polymer with the α,ω-functionalized polymer anion, followed by the addition reaction of PSLi with the DPE moiety in the backbone chain were actually repeated three times under the same conditions. The final α,ω-functionalized polymer anion was again changed to 10 000 g/mol in molecular weight.

The reaction processes were monitored by SEC. The SEC peaks of the polymers before and after the transformation reaction were always almost identical in shape and distribution. All of the linking and addition reactions were also found to proceed cleanly by the observations that the SEC profiles of the reaction mixtures always showed only two sharp distinct peaks corresponding to the linked products and deactivated living polymers used in excess in the reactions. In all of the reactions, their reaction efficiencies were estimated to be almost quantitative by comparing the peak areas of these two peaks. The intermediate polymers and objective graft (PS)s with three, four, and five PS branches could be isolated in 80 or higher % by fractional precipitation. These polymers are referred to as EG-2-D, EG-3-D, EG-4-D, and EG-3, EG-4, EG-5. As shown in Figure 4, the SEC profiles of all of the graft (PS)s herein synthesized exhibit sharp monomodal peaks without shoulders and tailings, and their peaks are gradually moved to higher molecular weight sides. The results are summarized in Table 2.

Agreement of the molecular weights between those calculated and those determined by SEC-RALLS was quite satisfactory in each polymer sample, and the molecular weight increased with repetition of the reaction sequence as expected. Their molecular weight distributions were very narrow, the M_w/M_n values being 1.03 or less as estimated by SEC. Accordingly, the expected structures and high degrees of molecular homogeneity of the resulting graft (PS)s are strongly indicated by these results. The positions

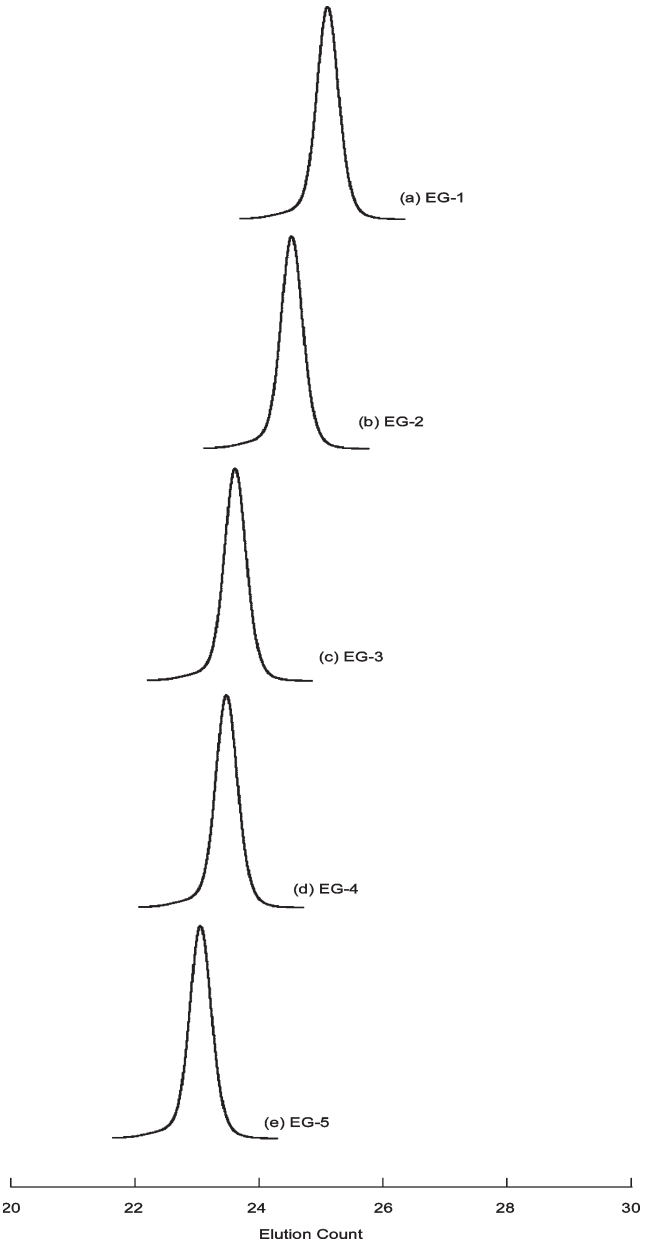


Figure 4. Size exclusion chromatographic profiles of a series of exact graft polystyrenes with one, two, three, four, and five PS branches (EG-1, EG-2, EG-3, EG-4, and EG-5, respectively).

of the branches and distances between the branches were precisely controlled by the molecular weights of the α,ω-functionalized polymer anions and could be intentionally changed by changing these molecular weights. As can be seen in Scheme 4, the final graft PS has the same SiOP group at the chain-end as other graft (PS)s, and therefore, the same process will be repeated to further synthesize the exact graft polymers with six or more branches. Thus, the excellence of the iterative methodology herein developed has been clearly demonstrated by the successful synthesis of exact graft (PS)s.

In the iterative methodology, the reaction sequence involving the three reaction steps works cleanly and quantitatively at least five times to successively synthesize a series of well-defined and expected exact graft (PS)s with up to five branches. The choice and setting of the three reaction conditions used in the reaction sequence are especially important to achieve successive synthesis. In this kind of stepwise synthesis, needless to say, the reaction inefficiencies and accidental mixing of impurities do not allow synthesizing such a series of pure and well-defined graft polymers.

In the previous methodology reported by Hadjichristidis et al., mentioned in Introduction, the backbone chain of the graft copolymer was prepared by using the initiation method with the DPE anion derived from a stoichiometric 1:1 addition of PSLi to the DPE terminus at each step. It may be rather difficult to keep perfect stoichiometry a number of times in practical experimental operation. Otherwise, undesirable polymers as side products are more or less produced, and the separation of the objective polymer from them in high yields becomes more difficult when repeating the reaction sequence. For this reason, the transformation reaction is newly added in the present methodology as an extra reaction step to avoid the above 1:1 addition reaction step. Because the next reaction site is prepared by the transformation reaction in each reaction sequence, it is possible to construct both the backbone and branch chains by using the termination method throughout all synthetic processes.

In each of the graft PS samples, the M_n value calibrated by SEC with standard PS samples was always lower than the absolute value determined by RALLS as expected from its branched architecture, and the deviation became more serious with increasing the branch number. However, the ratio of the M_n value observed by SEC using PS calibration with that by SEC-RALLS appears to be similar, around 0.8 in each sample. Since the final graft PS possesses five branches with similar M_n values (~10 000 g/mol), the distances between the branches are not equal to each other as listed in Tables 1 and 2. Accordingly, the final sample in addition to other exact (PS)s is not suitable a model graft polymer to discuss the effect of branch number as well as graft architecture on physical properties. The synthesis of exact graft (PS)s and copolymers with regularly spaced branch points is in progress.

Conclusions

In this article, the precise synthesis of a series of exact graft (PS)s with two, three, four, and five branches by a new iterative methodology based on the termination method by means of living anionic polymerization is described. By repeating the same reaction sequence involving the three reaction steps (transformation, linking, and addition reactions) five times, the above-mentioned exact graft (PS)s with up to five branches have been successively synthesized. In each of the samples, the molecular weights of both backbone and branch chains as well as the position and number of branch chains are precisely controlled as desired.

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